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RHEOLOGY OF CONCENTRATED SUSPENSIONS
OF SPHERES. II. HIGHLY CONCENTRATED
SUSPENSIONS AND PASTES

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II. HIGHLY CONCENTRATED SUSPENSIONS AND PASTES

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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 87, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites".

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Rheology of Concentrated Suspensions of Spheres

II. Highly Concentrated Suspensions and Pastes

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Abstract

A modified Stormer viscometer was used to study the flow behavior of suspensions of glass beads in liquids of different polarity over the volume concentration range from 50 to 60 percent. The flow behavior was pseudoplastic in some cases but rigid pastes were observed in other cases in this concentration range. The nature of the particle surface affected the flow behavior in the same manner as at lower concentrations (HPC 74-166). At still higher concentrations (> 60 v/o), a yield stress was found for all systems. Slipping occurred in the viscometer, and this phenomenon sets an upper limit for the study of concentrated suspensions.

Rheology of Concentrated Suspensions of Spheres

II. Highly Concentrated Suspensions and Pastes

Introduction

The flow behavior of very concentrated suspensions ($\phi > 50\%$) has not been studied intensively in the past. Reasons for this lack of attention are probably the difficulty in preparing the samples and the poor reproducibility of the data. Aside from these experimental difficulties, one is faced with suspensions which generally show non-Newtonian behavior in the concentration range considered. Several well-known equations, the Mooney equation (1) and the Simha equation (2), for instance, may not be suitable to use, for their derivations exclude any consideration of non-Newtonian behavior.

At high concentrations of solid particles, the amount of liquid is only enough to fill the interstices between particles, and the suspension gradually loses fluid-like characteristics and becomes a flowless paste. The mechanism of transferring stress continuously in a fluid breaks down in highly concentrated suspensions. Studies of powder rheology (3,4) indicate the occurrence of slip planes in a concentric cylinder apparatus which has radial baffle plates on the rotating cylinder. Since conventional viscometers all base their measurements at certain boundaries, a close look at what happens at these boundaries will enable us to know better the limitations of viscometers.

Materials and Methods

Glass beads ranging in size from 1 to 30 microns were suspended in liquids of differing polarity. The liquids were glycerol (polar), a polyol of slight polarity (Jefferson Chemical Company's Thanol SF 6500), and nonpolar low molecular weight polybutadiene (Lithium Company of America's Lithene PH). Two kinds of glass bead surfaces

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were examined -- cleaned but untreated and beads with a hydrophobic surface prepared by treating the surface with dimethyldichlorosilane. (More details on the beads, the liquids, and the surface treatments may be found in the first paper of this series.)

The highly concentrated suspensions were prepared by a method used by Landel et. al. (5). The glass beads and liquid were put into a polyethylene bag. Mixing was accomplished by kneading the bag with the hands. Finally, the mixture was placed under vacuum to eliminate trapped air bubbles.

The instrument used for the high concentration measurements was a modified Stormer viscometer (6). In this instrument unlike the Rotovisco the shear stress is a controlled variable. The shear stress was applied by adding weights to a string around a pulley attached to the inner cylinder and permitting their free fall through a vertical distance. The angular velocity was obtained by counting the time required for two or three revolutions. The true shear rates were calculated using the method suggested by Krieger and Maron (7). An advantage of this viscometer is that the yield stress can be measured directly by adding weights until the inner cylinder starts moving. To roughen the surface of the inner cylinder in later parts of the work, a layer of glass beads was coated around it by dipping the cylinder into a slurry of glass beads and Dupont's Duco cement diluted with acetone. The temperature was maintained at 25°C for all flow measurements.

Experimental Results and Discussion

Some flow curves of the systems studied are presented in Figures 1 through 4. Suspensions of beads treated with dimethyldichlorosilane

in glycerol were rigid pastes and were found to contain so much air that meaningful measurements could not be obtained. Therefore, this system was excluded from further study. Qualitatively, the mixture obtained looked like a flowless paste as contrasted to the suspensions of untreated beads and glycerol, which were free-flowing fluids. The untreated glass beads were wetted by the glycerol so that the beads tended to remain dispersed as individual particles. However, glycerol did not readily wet the silane treated beads, so the beads remained as agglomerates and the liquid could not penetrate the agglomerates to force out the air trapped inside them.

The flow curves indicate that the suspensions are pseudoplastic at high concentrations. The difference between the untreated glass bead suspensions and the silane treated glass bead suspensions observed in the previous work (8) is still present at concentrations above 50 volume percent beads. For a given shear rate, the shear stress was lower for the treated beads than for the untreated ones in either the nonpolar or the slightly polar liquids. As previously indicated, however, the treated beads in glycerol resulted in a rigid paste. At high rates of shear, the curves can be represented by straight lines. From the slopes of these straight lines, the viscosities η_{∞} at infinite shear rate can be calculated. The relative viscosities $\eta_{r,\infty}$ at infinite shear rate are given in Table I. The experimental relative viscosities are lower than that predicted by the Mooney equation ($\ln \eta_r = k\phi/(1-S\phi)$), which has parameters k and S equal to 2.5 and 1.35, respectively, but they are higher than predicted by the Thomas equation (9).

At still higher concentrations, approximately greater than 60 v/o, a yield stress can actually be measured with the modified Stormer viscometer. The origin of this yield behavior is probably the geometrical interlocking among the solid particles and between the particles and the cylinder wall.

It was noticed that in this highest concentration range the rotational speed of the inner cylinder of the viscometer was no longer constant at a given stress but varied with time. Usually, the angular velocities increased with time and showed a periodic pattern. One typical plot showing the variation of angular velocity with time is shown in Figure 5. To study this anomalous behavior further, the cup of the viscometer was filled with suspension up to the level of the upper surface of the inner cylinder. The motion of the suspension in the gap between the inner and the outer cylinders was detected by drawing a straight line across the gap with carbon black powder or red ink. At low shear stress, plug flow type behavior was observed at first. The movement of most of the suspension then slowed down to a stop, and shear occurred only in a very narrow region adjacent to the moving inner cylinder. The rotational speed of the inner cylinder gradually increased, and finally "slipping" occurred between the inner cylinder and the suspension. At high shear stress, slipping occurred immediately at the inner cylinder and no flow occurred. The periodic pattern of angular velocities was probably due to the stick-slip phenomenon occurring at the non-smooth slipping plane.

Since shear occurred in a very narrow region around the inner cylinder, it seemed probable that the surface roughness of the cylinder played an important role in the measurement. The inner cylinder was

coated with a layer of glass beads cemented to its surface to increase its roughness. The measured yield stresses were then compared with those measured with the uncoated cylinder. The results are shown in Figure 6. The yield stresses with the coated cylinder are considerably greater than those with an uncoated cylinder. The coated cylinder was able to support a large load, but slipping always occurred after the suspension yielded. However, on taking out the inner cylinder, we found that the surface was always coated with a layer of suspension, while the surface of the uncoated cylinder was clean without any suspension adhering to it. It seems that the slipping plane moved away from the surface of the inner cylinder to the bulk of the suspension when the cylinder was coated with glass beads. This is similar to what happens in a sheared powder bed. Because of the occurrence of a discontinuity in the suspension, the conventional stress-rate of shear concept is no longer applicable. The mixture of glass beads and liquid at these higher concentrations (> 60 v/o) is thus in a transition region between fluid-like suspension and free flowing powder. To study a mixture in this region will require the development of some novel techniques and apparatus.

Summary

Study of very concentrated suspensions shows that their flow behavior is pseudoplastic. The reason for this non-Newtonian behavior is not clearly understood yet. It may be related to the dense particle packing in the suspension. The surface characteristics of the solid particles are still important in these suspensions. At very high concentrations ($\phi > 60\%$), the yield stress can actually be measured with the viscometer. It is demonstrated that this yield

behavior is related to the mechanical interlocking between particles and the cylinder wall. Slipping occurs in this concentration range and the phenomenon observed indicates that the continuous structure of a fluid-like suspension breaks down when the volume concentration of solid exceeds 60%.

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Table I

Relative Viscosities of Suspensions at Infinite Shear Rates

Liquid	Glass Beads					
	Untreated Beads			Dimethyldichlorosilane Treated Beads		
	ϕ	η_{∞}	$\eta_{r,\infty}$	ϕ	η_{∞}	$\eta_{r,\infty}$
Glycerol	0.500	206	22.4	Rigid Pastes		
	0.525	333	36.2			
	0.548	412	44.8			
	0.549	470	51.1			
	0.574	1380	150.0			
	0.582	1630	177.0			
	0.600	3850	418.0			
Thanol	0.500	312	23.8	0.500	243	18.5
	0.550	575	43.9	0.550	604	46.1
	0.598	2450	187.0	0.600	2890	221.0
Lithere	0.500	513	20.2	0.501	513	20.2
	0.548	1280	50.4	0.550	1330	52.4
	0.580	2930	115.0	0.577	3250	128.0

Figures

1. Flow curves of suspensions of glass beads in Lithene.
2. Flow curves of suspensions of glass beads in Thanol.
3. Flow curves of suspensions of glass beads in Thanol.
4. Flow curves of suspensions of untreated glass beads in glycerol.
5. Variation of angular velocities of suspensions of untreated glass beads in glycerol. $\phi = 0.626$. Yield stress = 5700 dyne/cm^2 .
Measured at a shear stress of 8750 dyne/cm^2 .
6. Measured yield stresses of coated and uncoated viscometer cylinders.











